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**Efficient and product-controlled depolymerization of lignin oriented
by Raney Ni cooperated with $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$**

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ABSTRACT

A representative lignin was firstly prepared as well as an efficient lignin depolymerization process with highly controllable products was presented using Cs-substituted tungstophosphate (CsTP) cooperated with Raney Ni in this study. The double enzymatic lignin was depolymerized efficiently at 250–280 °C. The synergistic effects of Raney Ni with CsTP and temperature on the degradation of lignin were investigated by FT-IR, NMR, GPC and GC-MS techniques. Under the optimal condition at 270 °C for 3 h, the yield of depolymerized DEL was over 70 wt% and phenolic monomers were over 20%. The M_w of the lignin was reduced significantly from 15770 to 1150 g/mol (for aqueous phase lignin) and about 420 g/mol (organic phase lignin). In addition, indicating that this tandem catalyst facilitates the depolymerization and demethoxylation of lignin, but prevents hydrogenation of benzene ring of lignin to form cyclohexanols. More importantly, the formation of char was restrained effectively in this process.

Keywords: Lignin isolation, depolymerization, Raney Ni, Cs-substituted tungstophosphate

Introduction

Lignin constitutes for 10–35% (%weight) of lignocelluloses and carries the highest specific energy content (up to 40%) of all the three components (Zhang et al., 2011), meanwhile, it is considered as the most abundant, renewable and natural aromatic biopolymer on earth, which is industrially important starting material for the production of chemicals and fuels (Li et al., 2015). However, efficient transformation of lignin into value-added products is still a severe challenge due to complicated structure in lignin that possesses a wide variety of linkages, as compared to other two components (cellulose and hemicellulose) in lignocellulose. The most ideal reaction process would be able to effectively convert lignin into aromatic compounds without condensation (Li et al., 2015). Therefore, it is imperative to develop advanced catalytic reaction systems for the efficient and cost effective depolymerization of lignin.

Recently, a large number of researches focused on the lignin depolymerization and the yield and products selectivity varied with the reaction conditions and catalytic systems (Xu et al., 2014). Hydrogenolysis of lignin has been most frequently discussed in the scientific literatures in recent years and a variety of transition metals have been explored as catalysts for lignin depolymerization (Xu et al., 2014; Li et al., 2015; Song et al., 2012). Raney Ni catalyst was reported to be useful in the hydrogenolysis of lignin (Ferrini & Rinaldi, 2014; Jiang et al., 2015; Wang & Rinaldi, 2012a; 2012b). Some researches demonstrated a catalytic process for the hydrogenolysis of model substrates, bio-oils, as well as organosolv lignin involving

hydrogen transfer using isopropanol as hydrogen donor solvent (Ferrini & Rinaldi, 2014; Wang & Rinaldi, 2012a; 2012b). Raney Ni was found to be very active in transfer hydrogenation and hydrogenolysis reactions for upgrading bio-oils. In regard to real lignin feedstock, addition of acids allows the hydrogenolysis under mild conditions and accordingly enhances the depolymerization efficiency (Yan et al., 2008). Polyoxometalates, particularly the Keggin-type Cs^+ salts of polyoxometalates (e.g. CsTP) exhibit strong acidity and are well known for the catalytic transformation of cellulose into sugar alcohol (Chen et al., 2013; Deng et al., 2010; Geboers et al., 2010). Fortunately, dissociation energy (about 290 kJ/mol) of β -O-4 in lignin was lower than that (about 323 kJ/mol) of the glycosidic bond in cellulose, which was the lowest energy among all the chemical bond in cellulose (Parthasarathi et al., 2011). It will ensure that the CsTP solid acid catalyst also will efficiently cleave the aryl ether bond in lignin, especially β -O-4 linkage.

Inspired by the above research work for the depolymerization of biomass, Raney Ni cooperated with CsTP as tandem catalyst was selected to depolymerize a representative lignin sample, which is a residual lignin and prepared based on ball-milling and enzymatic hydrolysis process in this study. This strategy addresses the key challenge of yield loss of mono aromatic compounds owing to lignin recondensation, a major issue in acid-catalyzed depolymerization of lignin. In addition, the starting lignin with a high proportion of β -O-4 linkages will also facilitates the depolymerization process based on the existing results about depolymerization of lignin (Bouxin et al., 2015; Shuai et al., 2016).

2. Material and method

2.1. Material

Eucalyptus sawdust (40–60 mesh) was extracted with toluene/ethanol (2: 1, v/v) for 6 h to remove extractives, and then the extractive-free powder was dried at 60°C for 16 h. Chemical reagents were purchased from Sinopharm Chemical Reagent Beijing Co., Ltd, and the analytical chemicals used were purchased from Sigma-Aldrich. The liquid-state cellulase (Cellic[®] CTec2, 100 FPU/mL) was ungrudgingly supplied by Novozymes, Beijing, China.

2.2 Preparation of double enzymatic mild lignin (DEL)

To obtain a more representative lignin for lignin depolymerization, double enzymatic lignin (DEL) was firstly presented in this study. The detailed procedures for DEL were listed as follows. The ball-milling process was performed in a planetary ball mill (FritschGMBH, Idar-Oberstein, Germany) for 5 h. The ball-milled *Eucalyptus* sawdust (20 g) and 10.0 mL of Novozyme Cellulase (1000 FPU) were dispersed in acetate buffer (0.05 mM, 500 ml, pH 4.8) at 50 °C. Enzymatic hydrolysis was carried out in a rotary shaker at 150 rpm for 72 h. When enzymatic hydrolysis is completed, the mixture was separated and the residue lignin was washed with acidic water (pH=2.0), and then freeze-dried. The dried residual lignin was again undergone ball-milling for 5 h, then enzymatic hydrolysis as mentioned above. The isolation

procedure for DEL from *Eucalyptus* sawdust is vividly presented in Figure S1.

2.3 Catalyst preparation

The Cs salt of Keggin-type CsTP was prepared by the reaction between $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (HPW) and Cs_2CO_3 in aqueous solution. The 15 ml 0.02M Cs_2CO_3 was added into 20 ml 0.06 M HPW under vigorous stirring at 323K. Afterwards, the precipitates were obtained by filtration, followed by wash extensive with deionized water, and then calcined in air at 673 K for 2 h to obtain CsTP.

2.4 Lignin depolymerization

The catalytic depolymerization process of lignin was conducted in a 100 mL stirred E100 batch reactor. Typically, the reactor was charged with suspension of 0.5 g DEL, 0.5g CsTP and 0.5 g wet Raney Ni in 20 ml methanol/water mixed solution (v/v=1:1). The sealed reactor was purged with H_2 several times and the pressure was set to 3 MPa, then the sealed reactor was heated to the desired temperature under continuous stirring at 800 rpm within 3 h. After completion of the reaction, the reactor was cooled to room temperature with an ice water. Once the pressure was released, the pH value of the reaction slurry was adjusted to 2.0 by 1 M HCl. After that, the resulting mixture was filtered. The filtrated reaction mixture was extracted with ethyl acetate (15 mL \times 3). The organic phase lignin (OPL) were dried by rotary evaporation, while the aqueous phase lignin (APL) and the residue (char and catalyst) were freeze-dried. The bio-oil prepared under different temperatures was labeled as O₂₅₀,

O₂₆₀, O₂₇₀ and O₂₈₀, respectively. S₀ represents for the starting material (DEL).

2.5. Product characterization

NMR spectra of the lignin and depolymerized lignin samples were conducted at 298 K on a Bruker AVIII spectrometer (400 MHz) in DMSO-*d*₆ according to a previous literature (Wen et al., 2014). X-ray diffractograms was recorded using an XRD-6000 (Shimadzu, Japan). The diffraction pattern was obtained from 10° to 85° using Cu K α radiation ($k = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. The BET surface area of CsTP was measured by N₂ physisorption at 77K using a Micromeritics Tristar 3000 Surface Area and Porosimetry analyzer. Before measurements, the CsTP was out gassed 378K for 2 h. FT-IR spectroscopic measurements were conducted using a Nicolet iN10 FT-IR Microscope (Thermo Nicolet Corporation, Madison, WI, USA) in the region of 4000–800 cm⁻¹ with 64 scans. The weight average molecular weight (M_w) and number average molecular weight (M_n) of the lignin were determined by GPC as previously reported (Wen et al., 2014). The compounds in OPL were identified and quantified by injecting diluted samples into a GC-MS (Agilent 7890-5978, USA) and GC-FID (Agilent 7890, USA) using a 30 m \times 0.25 mm \times 0.25 μ m capillary column (HP-5MS), respectively. Gas chromatography was carried out at 50 °C for 10 min before the temperature was increased to 220 °C at 10 °C/min. The injector temperature was 220 °C in splitless mode. The components were identified by NIST 2011 spectral library and quantified using GC-FID by using external tetradecane standard.

3. Results and discussion

The newly-developed lignin preparation DEL was selected as a “model lignin” for the subsequent lignin depolymerization. The DEL is a residual lignin based on ball-milling and enzymatic hydrolysis, thus its β -O-4 linkages is abundant, similar to those of native lignin samples, such as MWL and CEL. To verify the structural characteristics of this lignin sample, the lignin obtained is subjected to 2D-HSQC NMR investigation. The main substructures of the lignin are shown in Figure 1 and all the annotated NMR assignments of lignin cross-signals in the HSQC spectra are based on a previous publication (Wen et al., 2014). As shown in Figure 1, the relative content of β -O-4 linkage in the DEL is 63.0/100Ar, while a little C-C linkage (e.g., β -5 and β - β) were observed (Figure 1). It is expected that the high proportion of β -O-4 linkage facilitates depolymerization of lignin according to a recent publication (Shuai et al., 2016). Furthermore, the average molecular weight (M_w) of the acetylated lignin was 15770 g/mol and the polydispersity index (PDI) was 2.07. As mentioned above, DEL was a native lignin (different from the industrial lignin, such as alkali lignin and organosolv lignin) to understand the structural transformations of real lignin in biomass during depolymerization processes.

The crystalline structures of HPW and CsTP were investigated by the XRD measurements. As shown in Table S1 and Figure S2, the XRD patterns of HPW and CsTP can be attributed to the cubic crystalline structure of Keggin-type polyoxometalate compounds, and the lattice structure did not undergo significant

changes after double-decompose reaction (Langpape et al., 1999; Zhang et al., 2010), suggesting that crystalline structures of HPW and CsTP are very similar. However, the surface areas of the CsTP sample sharply increased from 1.29 to 12.54 m²/g, which increased active surface area. It has been suggested that the substitution of the smaller hydrogen ions (H⁺) with larger cesium ions (Cs⁺) in the polyoxometalate can form the structure of mesopores and micropores (Zhang et al., 2010).

Based on the proposed depolymerization processes, the yields of products (OPL, APL and char) and molecular weight of the degraded lignin (OPL, APL) were shown in Table 1. It can be observed that the yields of OPL and APL were dramatically improved for lignin as the depolymerization temperature rose, while the char yield was sharply decreased to zero. Importantly, molecular weight of the degraded lignin was sharply reduced from 15770 to less than 1200 g/mol after depolymerization process. The phenomenon implied that this catalyst system could inhibit formation of char by recondensation during depolymerization, which greatly promoted the depolymerization of lignin. The yield of APL increased from 12.46 to 18.18 % with the temperature increasing from 250 to 260 °C, while its yield decreased to 15.16% with the temperature further elevating to 270 °C. Meanwhile, the yield of OPL reached maximum. However, the yield of the OPL decreased from 77.54 to 67.46 when the reaction temperature was higher than 270 °C. These results were attributable to the fact that oligomeric lignin was firstly started forming and then degraded into monomeric lignin, and some of which were decomposed to volatile organic compounds when the temperature exceeded 270 °C.

The FT-IR spectra of original lignin and OPL were analyzed for qualitatively monitoring the changes in functional groups according to the literatures (Faix, 1991; Mahmood et al., 2015). As shown in Figure S3, the peaks of phenolic or aliphatic OH, methyl and methylene groups became weaker after depolymerization due to dehydration and demethylation during hydrogenation process. Besides, the intensity of unconjugated ketones decreased after hydrogenation process, which was due to the reduction of ketones. The ether linkages at 1165 cm^{-1} was weaker in spectra of OPL as compared to DEL, implying that the majority of the ether linkages (e.g., β -O-4) were cleaved. Meanwhile, the bands corresponding to aromatics at $1400\text{--}1700\text{ cm}^{-1}$ remain almost the same between original lignin and OPL, implying that the depolymerization process did not change lignin's aromaticity.

^1H NMR spectra of the samples and the integration results are shown in Table S2 and Figure S4, in which the relate resonances were assigned based on the previous publications (Jahan et al., 2007; Wen et al., 2014). As shown in Figure S4, the proton peaks of DEL are smooth while that of OPL are keen-edged, which may be caused by the depolymerization of DEL. In this case, the macromolecules were degraded into small molecules and therefore the molecular weights sharply decrease. Additionally, the signals of aliphatic units rapidly increased and that of the ether bond sharply decreased as the temperature rose. The reason for this phenomenon could demonstrate that a large number of aryl-*O* and aryl-*O*-alkyl bonds were subject to rupturing and small molecular aliphatic compounds were generated. Besides, the content of ArH remained nearly unchanged, implying that there was no excessive use of H_2 to form

cyclohexanols.

To further understand the effect of the depolymerization temperature on lignin depolymerization reactions, the OPL was analyzed by GC-MS technique. Figures 3, 4 and Table 2, S3 illustrate the effect of the depolymerization temperature on the yield and distribution of the degraded monomer. The degraded products are categorized in six classes, namely phenols, guaiacols, syringols, benzene derivative, cyclohexanes and other volatile chemicals. As shown in Figure 2, yield of the degraded monomers was firstly increased from 13.4 to 22.4% based on an increase of the temperature from 250 to 270 °C, while decreased to 20.8% at 280 °C. It suggested that higher temperature was in favor of lignin depolymerization, but a higher temperature of 280 °C would result in a further decomposition of the degraded monomers to form small-molecule gases. The monomeric products included phenols, guaiacols, benzene derivative, and a small amount of syringols, cyclohexanes and other volatile chemicals. Moreover, the yield of phenols, guaiacols, benzene derivative increased with the raise of temperature. In contrast, the yield of the syringols decreased as the temperature increased. Besides, the content of cyclohexanes was very littler and remained nearly constant. Based on the monomeric-product distribution (Figure 2), it can be concluded that the tandem catalyst showed low ring-hydrogenation activity and good demethoxylation in all of the cases. Figure 3 shows GC-MS results of the monomeric-products performed at various reaction temperatures. It was found that the main monomeric products were similar and compounds 6 and 7 were the main degraded product at various depolymerization temperatures, which showed satisfied

catalytic selectivity. As the temperature rose, the γ -CH₃ of part aromatic compound 3 was eliminated and formed aromatic compound 3, implying that the tandem catalyst also has the ability of demethylation. In short, DEL can be effectively degraded into eight kinds of aromatic compounds in this tandem catalytic system. However, further optimization experiment is under way in our lab.

4. Conclusions

An efficient tandem catalysis approach for cleavage of β -O-4 linkages in a novel native lignin models has been proposed and developed, involving ether hydrolysis by CsTP solid acid followed by upgrading by Raney Ni. By depolymerization, the molecular weight of the DEL was reduced significantly from 15770 to about 1000 g/mol (for APL) and about 400 g/mol (OPL). Meanwhile, there were few chars formed. Besides, it was found that the temperature only affects the yield of the degraded monomers, but don't changes of the distribution of the degraded monomers. In short, this tandem catalyst exhibited a good catalytic performance and selectivity.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at

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